A THIN-FILM SOLID-ELECTROLYTE FUEL CELL

A. O. Isenberg
W. A. Pabst
E. F. Sverdrup
D. H. Archer

Westinghouse Electric Corporation
Research Laboratories

ABSTRACT

The chemical energy of coal can be directly converted into electrical energy by solid-electrolyte fuel cells. These fuel cells operate at about 1000°C and use a doped-zirconia solid electrolyte. A thin-film, solid-electrolyte cell has been fabricated by successively applying: 1) a porous fuel electrode; 2) a dense, continuous yttria doped zirconia electrolyte; and 3) a porous air electrode layer on a porous ceramic tube 1.3 cm in diameter and 5 cm long. Each of these three layers was less than 30 μ thick. The electrolyte was produced by chemical vapor deposition and the electrodes by sintering processes.

The cylindrical cell was tested with H_2 (~ 3% H_2O) fuel gas inside and air outside the tube. The open circuit voltage of the cell was 1.06 volt -- within 2% of the theoretical value. The operating voltage was 0.73 volt at 517 milliamperes/cm^2. The resistive losses checked closely those calculated from the resistivity and thickness of the electrolyte and the resistance of the electrodes. The polarization losses were less than 0.10 volt for the porous cobalt-zirconia fuel electrode and a 0.20 volt for the air electrode. While the performance of the cell thus exceeds that projected for an initial 100-kilowatt coal-burning fuel-cell power plant, further work is required to improve the air electrode and to interconnect such thin-film cells in a battery.

Work sponsored by the Office of Coal Research, U. S. Department of the Interior -- N. P. Cochran and P. H. Towson, Contract Monitors.

A THIN-FILM SOLID-ELECTROLYTE FUEL CELL

A. O. ISENBERG
W. A. PABST
E. F. SVERDRUP
D. H. ARCHER

WESTINGHOUSE ELECTRIC CORPORATION
RESEARCH LABORATORIES
PITTSBURGH, PENNSYLVANIA 15235

A THIN-FILM SOLID-ELECTROLYTE FUEL CELL

A. O. Isenberg
W. A. Pabst
E. F. Sverdrup
D. H. Archer

Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

ABSTRACT

The chemical energy of coal can be directly converted into electrical energy by solid-electrolyte fuel cells. These fuel cells operate at about 1000°C and use a doped zirconia solid electrolyte. A thin-film, solid-electrolyte cell has been fabricated by successively applying: 1) a porous fuel electrode; 2) a dense, continuous yttria doped zirconia electrolyte; and 3) a porous air electrode layer on a porous ceramic tube 1.3 cm in diameter and 5 cm long. Each of these three layers was less than 30μ thick. The electrolyte was produced by chemical vapor deposition and the electrodes by sintering processes.

The cylindrical cell was tested with H_2(~3% H_2O) fuel gas inside and air outside the tube. The open circuit voltage of the cell was 1.06 volt -- within 2% of the theoretical value. The operating voltage was 0.73 volt at 517 milliamperes/cm^2. The resistive losses checked closely those calculated from the resistivity and thickness of the electrolyte and the resistance of the electrodes. The polarization losses were less than 0.10 volt for the porous cobalt-zirconia fuel electrode and a 0.20 volt for the air electrode. While the performance of the cell exceeds that projected for an initial 100-kilowatt coal-burning fuel-cell power plant, further work is required to improve the air electrode and to interconnect such thin-film cells in a battery.

INTRODUCTION

Electrical energy can be generated using coal as a fuel by direct electrochemical conversion using solid electrolyte fuel cells.[1] A solid electrolyte fuel cell can be visualized as shown in Figure 1. The oxygen receives electrons at the air electrode (cathode), migrates through the electrolyte as an ion and transfers the electrons at the fuel electrode (anode) reacting with the fuel gas to form H_2O and CO_2. The electrolyte is a yttria doped zirconia which has an oxygen ion transfer number very close to one. The electrodes are either metallic or consist of electronically conducting oxides. This fuel cell operates at temperatures near 1000°C where the oxygen ions are mobile. A fluidized coal bed, receiving heat from the fuel cells, gasifies the coal and generates the fuel for the cells. Since the goal of this work is central station power, the fuel cell power plant has to compete with conventional power generating plants. This means that the solid electrolyte fuel cells have to be fabricated using low cost production techniques and that the costs of expensive materials (i.e. the yttria doping of the electrolyte) have to be minimized. The thin-film fuel cell

Work sponsored by the Office of Coal Research, U.S. Department of the Interior -- N. P. Cochran and P. H. Towson, Contract Monitors.

represents an important step toward this goal. To prepare such thin film fuel cells complex ceramic machining and assembling techniques[2] are replaced by a less expensive film deposition process. The reduction of electrolyte thickness from nearly 1000 microns to about 30 microns reduces the calculated cell resistance from 1Ω to about 3 x 10^{-3}Ω per square centimeter of active cell area at the operating temperature. This paper reports the construction and performance of a thin-film fuel cell.

CELL PREPARATION

The cell was built on a cylindrical porous ceramic support tube coated first with the fuel electrode, then the thin film electrolyte, and finally by the air electrode. The fuel flows through the inside of the tube and diffuses through the porous structure of the support tube to the fuel electrode. Combustion products diffuse in the opposite direction. A concentration gradient is built up with increasing combustion product content along the tube axis. Air flows over the outside air electrode.

As support tube for the cell we used a 1.3 cm O.D. stabilized zirconia tube with a wall thickness of 1.5 mm. The measured open porosity of the support tube was 15 percent.

The tube was covered over a length of nearly 15 cm with a fuel electrode consisting of a 20 to 30μ thick cobalt-zirconia cermet layer. This layer was applied by sintering.

The fuel electrode was covered with a thin film electrolyte by chemical vapor deposition.

The x-ray analysis of the electrolyte films confirmed a fully cubic structure of the electrolyte.

Film thicknesses obtained from a three hour chemical vapor deposition run are about 30μ to 50μ. Cross section analysis of various films grown in a number of experiments show that pores up to 10 microns in the cermet fuel electrode can be bridged with a gas-tight electrolyte film.

After the electrolyte film was applied to a 4 cm long cell it was assembled into the tester for testing at 950°C. As Figure 2 shows, alumina adapter tubes fit over the cell tube ends. Gold washers seal the cell tube to the alumina tubes. The assembly was compressed by means of an alumina rod running through the center of the tubes. Threaded brass tubing was glued to the alumina rod ends to allow the tubes to be placed under a controlled compression using a spring on one end of the assembly. Since the gold washers are pressed against the thin fuel electrode located between support tube and thin-film electrolyte, they provide electrical contact to the fuel electrode. A platinum wire was welded on to one washer representing a potential probe and a 1.5 mm thick palladium silver wire was welded to the other washer as current lead to the fuel electrode.

An air electrode consisting of a three layer coating of platinum was applied in three separate sintering steps. The platinum was sintered in air while the inside of the cell was purged with forming gas. The platinum air electrode was backed up with a platinum screen current collector. A 1.5 mm thick palladium silver wire acted as the current lead on the air side of the cell.

The cell was equipped with a thermocouple which acted also as a potential probe for the air electrode. An electrolyte reference electrode was placed beside the air electrode. Figure 3 shows the cell. The total active cell area, determined by the air electrode size, was 5.8 cm^2. A cross section through the thin film cell structure is shown in Figure 4.

EXPERIMENTAL RESULTS

The cell was tested using hydrogen containing nearly 3% water as the fuel. The flow rate indicated by flowmeters was 400 to 500 ccm per minute. Air was supplied by natural convection to the outside of the cell.

The cell was operated at 950°C. The electrical characteristics are shown in Figure 5. The polarization characteristics of the fuel and the air electrode include the ohmic and non-ohmic part of the polarization. The measured open cell voltage was 1060 mV over the entire test period of nearly 100 hours. A maximum current density of 720 mA/cm^2 was obtained at a cell voltage of 618 mV. The cell was operated for a 96 hour test at a continuous current load of 500 mA/cm^2. The cell voltage at this current level is plotted versus time in Figure 6.

Current interruption tests[3] showed an ohmic potential drop in the cell of 30 mV at a current density of 630 mA/cm^2. The resistance drop in the fuel electrode, calculated from the square resistance of the fuel electrode, does not exceed 5 mV at this current level. The resistance of the air electrode was neglected because of the heavy current collector. The difference of 25 mV is due to the potential drop in the electrolyte.

From these data, the calculated resistivity of the thin film electrolyte is:

$$\rho[\Omega\cdot cm] = \frac{0.025}{0.630 \times 30 \times 10^{-4}} \left[\frac{V\cdot Cm^2}{A\cdot cm}\right] = 13\ [\Omega\cdot cm]$$

This compares very favorably with the resistivity of sintered zirconia doped with 10 mole percent yttria which is between 11 and 12 ohm centimeters at this temperature.

SUMMARY

A high temperature fuel cell using a thin-film zirconia electrolyte, prepared by chemical vapor deposition, was tested successfully under current load in a single cell design. The test proved the gas tightness of the electrolyte. Resistive losses checked closely with those calculated from the resistivity and thickness of the electrolyte and resistance of the electrodes. The tested cell was thermally cycled four times without damaging the thin film structure. The performance of this single cell exceeds that required for the initial 100-kilowatt coal-burning fuel-cell power plant. Fuel electrode tests indicate that thin-film fuel cells will perform equally well on the fuel gas derived from the fluidized coal bed used in that plant.

The development of the thin-film fuel cell is an important step toward a commercial power generating system capable of producing electrical energy from coal at overall efficiencies approaching 60 percent. Further work is required to provide the thin-film cells with low-cost air electrodes and to interconnect them in batteries.

REFERENCES

(1) Zahradnik, R. L., Elikan, L., and Archer, D. H., "A Coal-Burning Solid-Electrolyte Fuel Cell Power Plant," ADVANCES IN CHEMISTRY SERIES, Number 47, page 343, 1965.

(2) Ibid.

(3) Sverdrup, E. F., Archer, D. H., Alles, J. J., Glasser, A. D., "Testing of Electrodes for High-Temperature, Solid-Electrolyte Fuel Cells," Hydrocarbon Fuel Cell Technology, Academic Press Inc., New York, 1965.

Dwg. 859A486

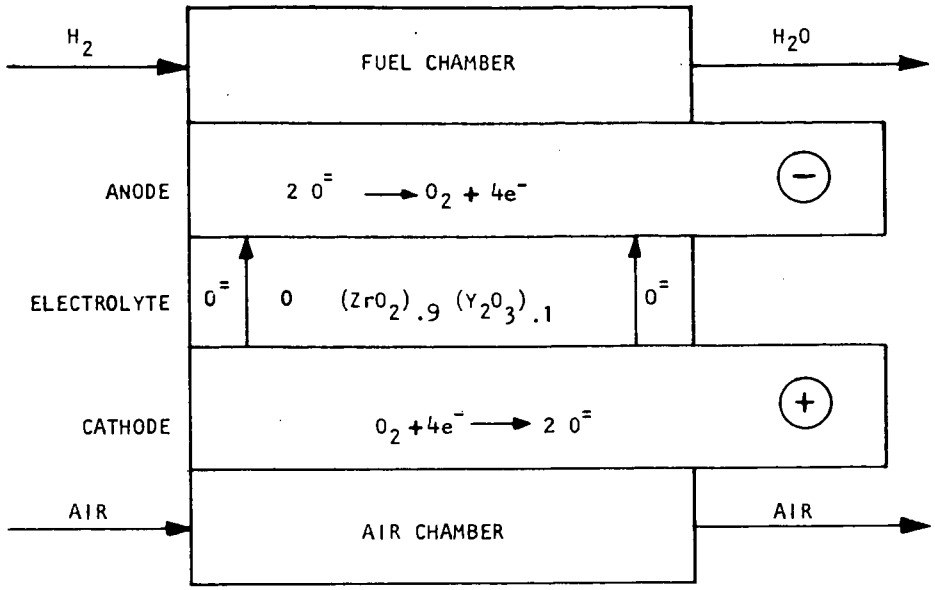

FIG. 1 OPERATING PRINCIPLE OF A SOLID ELECTROLYTE FUEL CELL

Dwg. 859A485

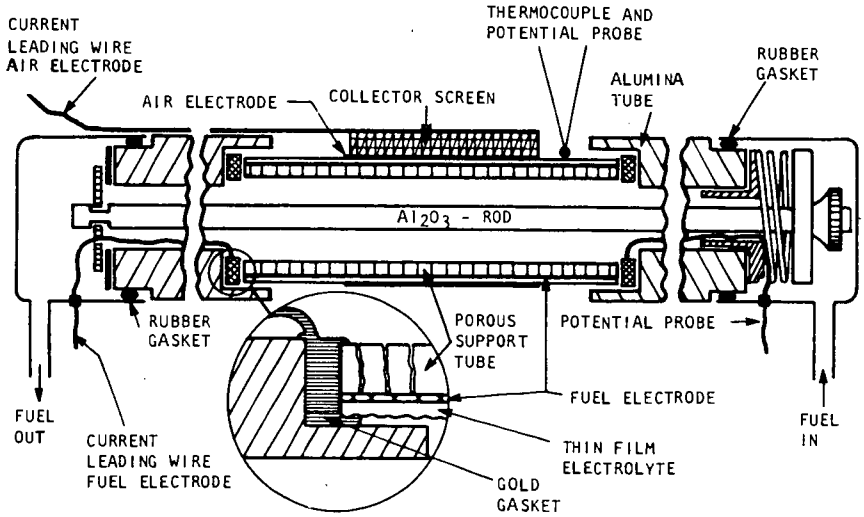

FIG. 2 TEST ARRANGEMENT FOR A THIN FILM ELECTROLYTE FUEL CELL

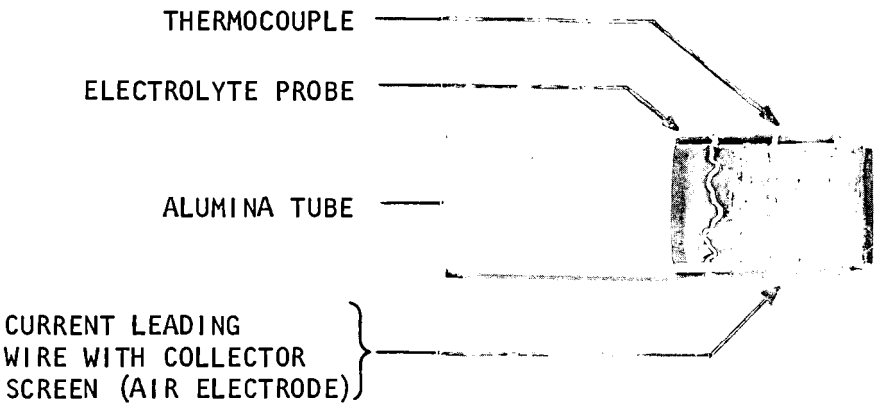

FIG. 3 ASSEMBLED THIN FILM ELECTROLYTE FUEL CELL

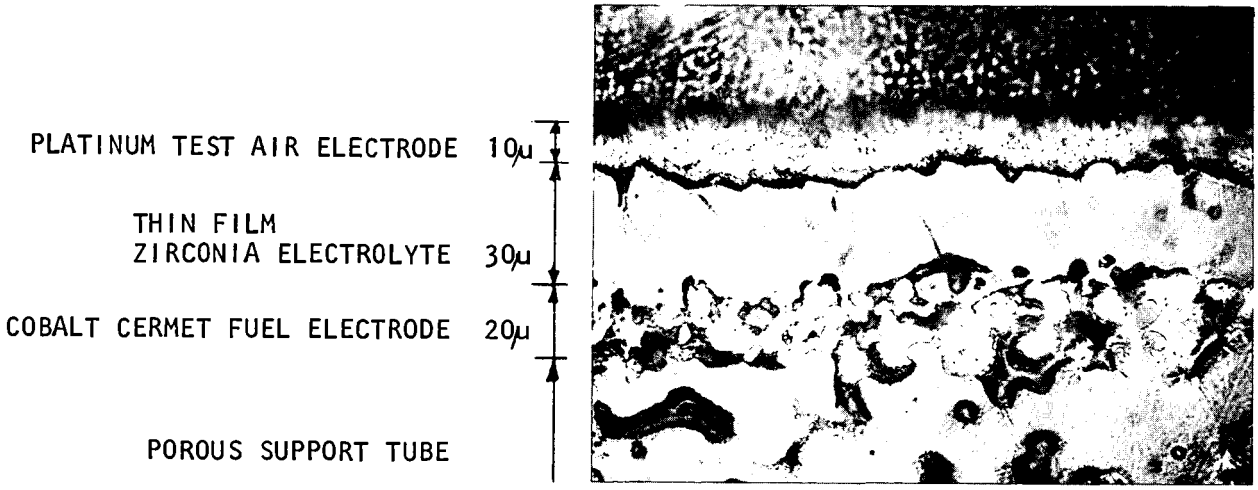

FIG. 4 CROSS SECTION THROUGH A THIN FILM
ELECTROLYTE FUEL CELL AFTER OPERATION

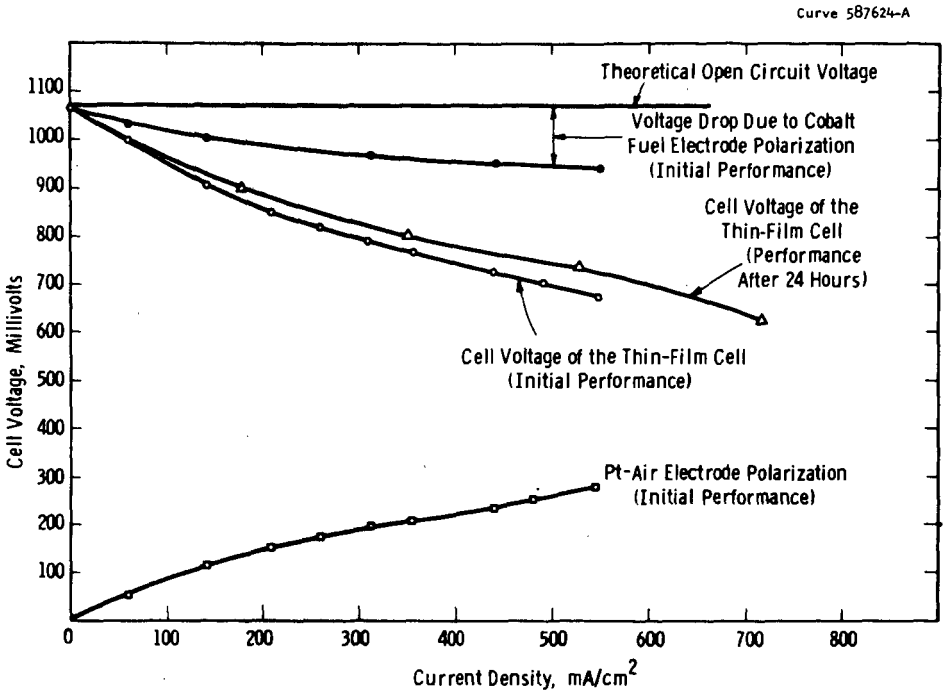

FIG. 5 PERFORMANCE OF A THIN FILM FUEL CELL AT 950°C WITH H_2+ 3% H_2O AS FUEL AND WITH AIR

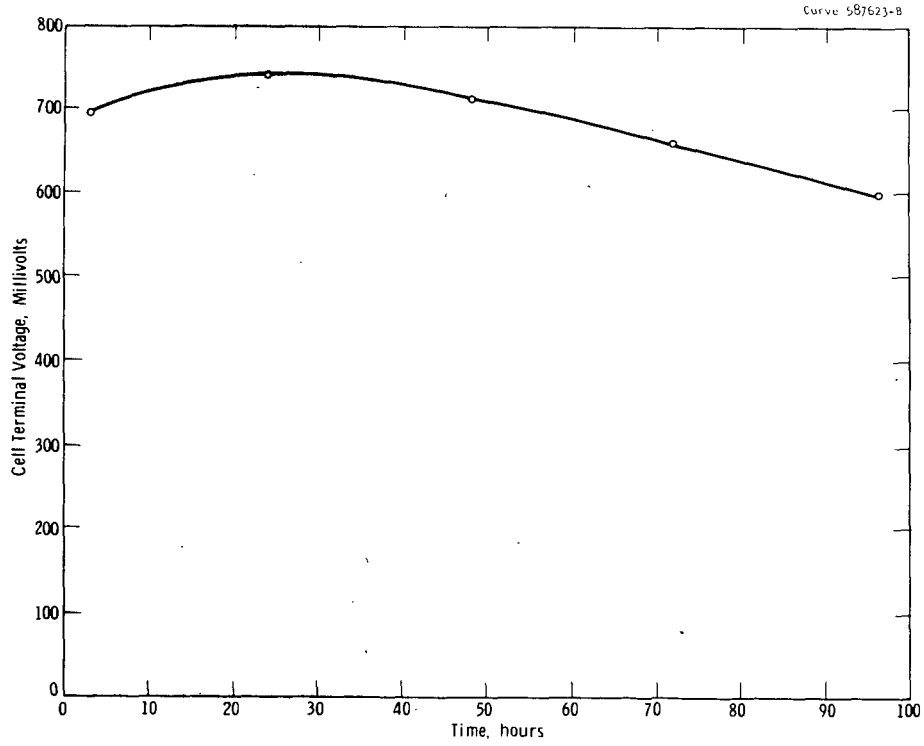

FIG. 6 TIME DEPENDENCE OF CELL PERFORMANCE (CELL VOLTAGE AT A LOAD OF 500 mA/cm^2)